Synthesis and Upgradation of Castor seed bio-oil using Catalytic cracking

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ABSTRACT

Global energy crisis and increasing energy demand has focused attention to alternative resources. Biomass resources can be considered as solution for this crisis. The bio-oil obtained from biomass has some major draw backs such as high water content, acidity and lower hating value. Catalytic pyrolysis shows the potential to satisfy the demand for bio-oil with an improved quality. Most of the research work supported by zeolite catalyst for upgrading bio-oil. Although researchers found good quality of oil, still they suffer from catalyst de-activation, coke formation, and generation of higher gas yields. Up on surveying the literature, it was found that much work has not been done using basic catalysts. In the available literature also, it was mentioned that Calcium Oxide works well for biomass vapor upgradation. Based on this finding, Calcium oxide is chosen as catalyst in our study.

In the present work catalytic pyrolysis of caster seed oil was carried out over CaO catalyst. The catalyst was activated at 650 ^{0}C and characterized by X-ray diffraction, SEM and studied their morphological structure. Pyrolysis experiments were performed in a semi-batch reactor with Nitrogen purging and without Nitrogen purging at various temperatures (450, 500, 525 ^{0} C), with a constant heating rate of 20^o C/min and various catalyst to oil ratio (1:4, 1:9, 1:12) respectively. The liquid obtained from catalytic pyrolysis of caster seed oil with Nitrogen purging at different catalyst ratio was compared with the liquid obtained without nitrogen purging at different catalytic ratios were characterized by FTIR and physical properties analysis. Upgraded bio-oil registered higher calorific value than raw pyrolytic oil. Nitrogen purging resulted higher oil yields and calorific value, of which the highest yield of 56.6% was obtained at 500 ^{0} C, with catalyst to oil ratio 1:9.

Keywords: Pyrolysis, Cracking of hydrocarbons, Char, Purging.

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NOMENCLATURE

ACOL – Activated olivine

RAWOL- Raw Olivine

ACSE- Activated Serpentine

RAWSE- Raw Serpentine

ALU – Alumina

S/N – Signal to Noise ratio

OLP – Organic Liquid Product

FWHM- Full width at half maximum

EFB- Empty fruit branch

ASTM- American Society for Testing and Materials

WHSV- Weight Hourly Space Velocity

CHAPTER-1

INTRODUCTION

1. Introduction

1.1.Present energy scenario

Today, the world runs on fossil fuels. The main cause for rapid development in 20th century is undoubtedly this mysterious energy treasure, the petroleum. It has affected the lives of people from dawn to dusk, from energy to medicines, plastics, chemicals... These are just a few and the total tally is unending. And therefore there is no wonder in saying 'Petroleum drives human lives'. This has even changed geopolitical sphere of the world, making some of the once called barren lands –deserts, as the richest places on the planet.

If we look the present supply of global energy from various sources, still the fossil fuel dominates the supply with oil is the largest source with around 32% share, followed by coal and natural gas.

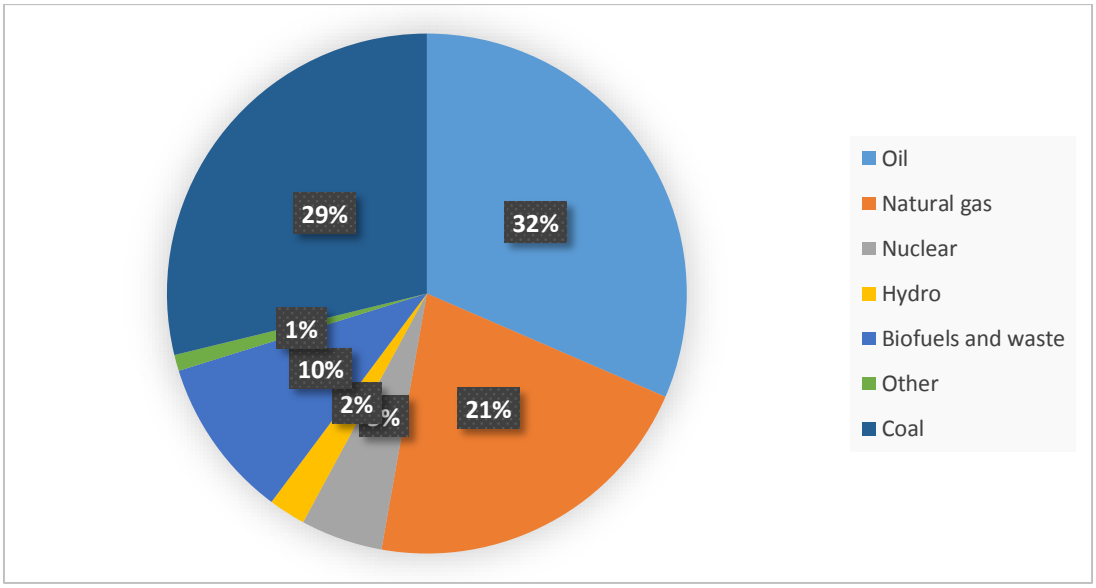

Figure 1: Total world energy supply by source in 2011
Source: Key world energy Statistics, IEA

1.2.Problems with conventional fuels

1.2.1. Petroleum

Although it is greatest energy provider, the major hurdle is availability. Due to rapid utilization and very slower rate of generation of petroleum in deeps of earth, its availability is a high concern. Now a days, although many wells are explored for oil, few of them only contain

significant quantities of oil. In addition, the crude extraction and refining is a complex task and releases a lot of pollutants.

1.2.2. Natural gas

Nearly all natural gas extraction today involves a technique called hydraulic fracturing, or fracking, in which dangerous chemicals are mixed with large quantities of water and sand and injected into wells at extremely high pressure. Fracking is a suspect in polluted drinking water in various parts of the world. Also, the handling of wastewater is also a complex task.

1.2.3. Nuclear energy

Nuclear energy is a cheap as well abundant. But, many accidents in nuclear plants like Chernobyl, Fukushima are raising concerns over safety of nuclear energy. Moreover, nuclear waste disposal is the most difficult and currently no effective technology has been developed to handle this. So, developed countries like Germany have already made it clear that they wish to free from nuclear power.

1.2.4. Coal

This has been in use from around three hundred years. Owing to its low energy density, large quantities of coal are required to fulfill current day needs. It also causes problems with mining, transportation. Burning coal also releases toxic gases and large amounts of waste like fly ash. Its disposal is a tough task and researchers are working on using it as a construction material. Still, it is a distant dream to to produce clean energy from coal.Due to problems of pollution and safety, these conventional power plants are facing stiff opposition from public and acquisition of land became a hectic task for governments.

1.2.5. Renewable energy

These are abundant, clean, nature replenishes them continuously using various phenomena. Hydro power is although cheap, requires large pieces of land for construction of projects. Geothermal, wind, tidal, solar energy etc…account for little contribution, in development phase and are uneconomical for present day.

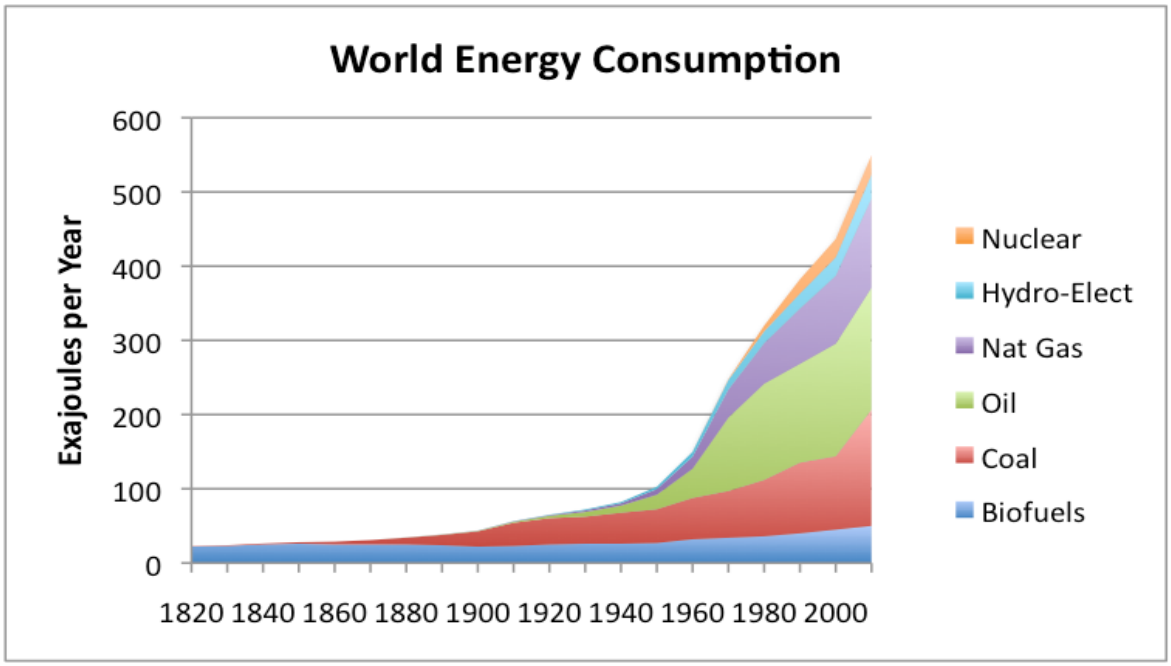

Figure 2: World primary energy sources- past to present

In this context, we need to choose a reliable and renewable energy source for future needs and situations. Taking into consideration the little availability of fossil fuels, developmental phase of other renewable sources, biomass can be considered as potential fuel source. It was the only source from centuries and is highly abundant on the planet.

1.2.6. Biomass energy

Biomass is biological material derived from living, or recently living organisms. In the context of biomass for energy this is often used to mean plant based material, but biomass can equally apply to both animal and vegetable derived material. Biomass is carbon based and is composed of a mixture of organic molecules containing hydrogen, usually including atoms of oxygen, often nitrogen and also small quantities of other atoms, including alkali, alkaline earth and heavy metals. These metals are often found in functional molecules such as the porphyrins which include chlorophyll which contains magnesium.

Although it is thought that biomass combustion causes rise of CO2, it is a myth, since biomass takes CO2 while it is growing, and releases when burnt. That in turn will be taken by replanted biomass. Hence, total CO2 liberated into atmosphere is zeroed carbon cycle is completed.

1.2.6.1.Categories of biomass materials

Within this definition, biomass for energy can include a wide range of materials.

There are five basic categories of material:

- ✓ **Virgin wood:** from forestry, arboricultural activities or from wood processing
- ✓ **Energy crops**: high yield crops grown specifically for energy applications
- ✓ **Agricultural residues**: residues from agriculture harvesting or processing
- ✓ **Food waste**: from food and drink manufacture, preparation and processing, and post-consumer waste
- ✓ **Industrial waste and co-products:** from manufacturing and industrial processes.

CHAPTER-2

LITERATURE REVIEW

2. Literature review

2.1.Biomass to biofuel conversion

Although the biomass is abundant, its energy density is much lower than fossil fuels. For this reason, it needs to be converted to other forms such as liquid or gas, which can be further utilized to produce heat. The basic conversion routes are:

2.2.Bio- chemical conversion

As biomass is a natural material, many highly efficient biochemical processes have developed in nature to break down the molecules of which biomass is composed, and many of these biochemical conversion processes can be harnessed. Biochemical conversion makes use of the enzymes of bacteria and other micro-organisms to break down biomass. In most cases micro-organisms are used to perform the conversion process:

2.2.1. Anaerobic Digestion

It this process, plant and animal materials (biomass) are broken down by micro-organisms in the absence of air. It happens in three steps.

1. When biomass is kept inside a digester, anaerobic digestion starts.
2. Naturally occurring micro-organisms digest the biomass, which releases a methane-rich gas (biogas). Methane can be used to produce heat and power.
3. The remaining material (digestate) is rich in nutrients, which can be used as a fertilizer.

Many forms of biomass are suitable for anaerobic digestion; including food waste, slurry and manure, as well as crops and crop residues. However, woody biomass cannot be used in anaerobic digestion due to the presence of lignin, which the microorganisms can't breakdown.

2.2.2. Fermentation

Fermentation is the process by which microorganisms such as yeast and bacteria convert organic molecules into other products. For biofuels the typical useful fermentation products are Butanol and ethanol, which can be used as liquid transport fuels. Biomass is converted to alcohols and other solvents by microorganisms. Fermentations occur in the absence of oxygen. Yeasts can be used to produce ethanol. Solventogenic clostridia are bacteria can be used to produce hydrogen gas, Acetone, Butanol and Ethanol. Butanol is the main

product. Yeasts are more tolerant to alcohol and therefore produce more than bacteria, however often the bacteria are capable of using a wider range of substrates.

2.2.3. Composting

This is similar to anaerobic digestion, though making use of different bacteria, composting is the aerobic decomposition of organic matter by microorganisms. Usually, dry materials are used for composting.

2.3. Thermal conversion

These are processes in which heat is the dominant mechanism to convert the biomass into another chemical form. The basic alternatives are separated principally by the extent to which the chemical reactions involved are allowed to proceed:

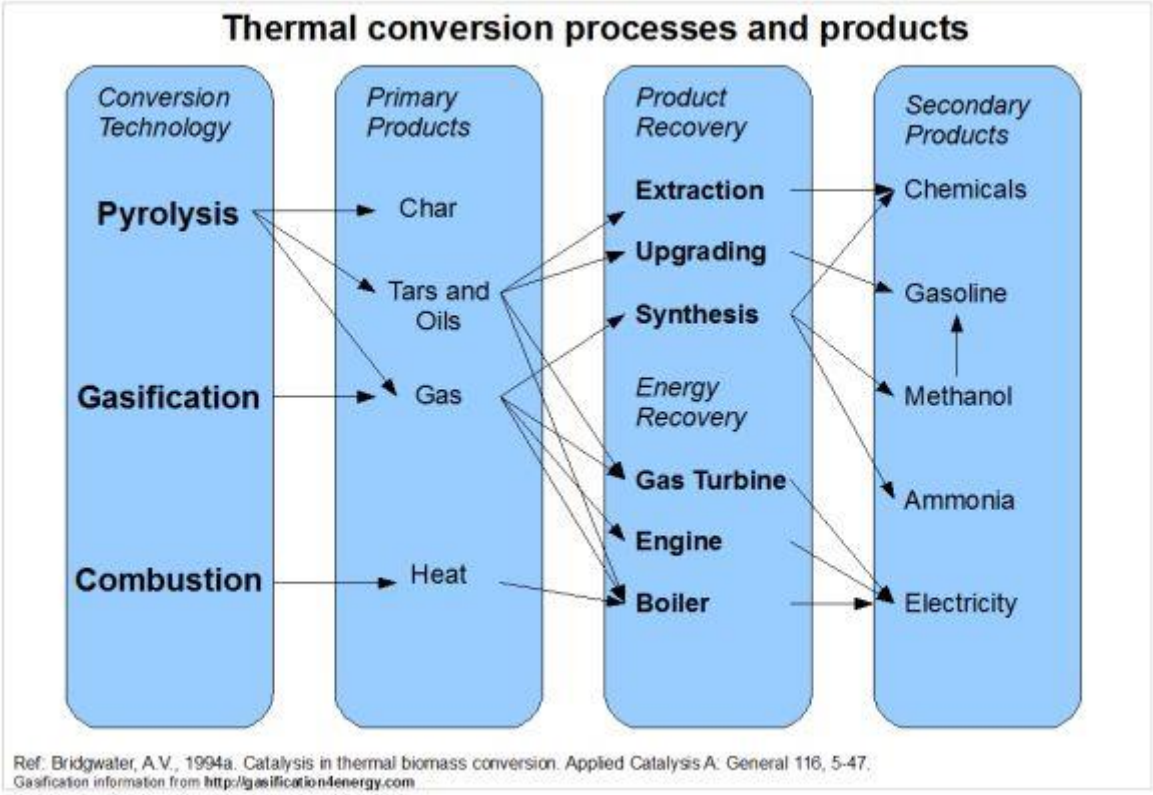

Figure 3: Thermal conversion processes and products

2.3.1. Combustion

Combustion is the simplest, ancient method to produce heat energy. In a combustion reaction, combustible material like biomass reacts with oxidizer like oxygen to produce Carbon dioxide and water.

2.3.2. Gasification

Biomass gasification is incomplete combustion of biomass requiring lesser amount of oxygen than combustion. It results in production of combustible gases consisting of Carbon monoxide, Hydrogen, and traces of Methane. This mixture is called producer gas. Producer gas can be used to run internal combustion engines, can be used as substitute for furnace oil in direct heat applications. Methane can also be used to produce methanol, – an extremely attractive chemical in an economical way. Since any biomass material can undergo gasification, this process is much more attractive than ethanol production or biogas where only selected biomass materials can produce the fuel.

2.3.3. Thermal Pyrolysis

Thermal Pyrolysis or simply pyrolysis is a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen. It involves the simultaneous change of chemical composition and physical phase, and is irreversible. Pyrolysis involves a complex set of reactions that decompose organic matter into an H-rich volatile fraction of vapours, aerosols and gas, and a C-rich solid fraction. The reaction products are generally classified as bio-oil, bio-char and bio-gas, and the product yields can be modified by changing the process conditions such as heating rate, temperature and residence time. Commonly, high heating rates are used to maximize the oil fraction because of the poor thermal conductivity of biomasses, together with temperatures over 500 ^{0}C and residence times if 1-2 sec. Pyrolysis is generally classified as slow, fast, medium, and flash pyrolysis.

Table 1: Types of pyrolysis and major applications

Pyrolysis type	**Heating rate**	**Residence time**	**Main product application**
Slow	Low	High	Charcoal production
Medium	Medium	Medium	Liquid production
Fast, Flash	High	low	Gasification

Singh et.al have performed slow pyrolysis of castor seed in a Stainless steel batch reactor at various temperatures in the range 450- 600 ^{0}C [1]. In Castor seed TGA study, it was observed that intermediate associations among were broken in second phase pyrolysis, and stronger bonds were destroyed at higher temperatures. They collected aqueous and organic phase products after pyrolysis and found that at 550 ^{0}C, highest yield of castor seed bio-oil was obtained. In the product bio-oil, alcohol, phenols, ketones, esters, alkenes, alkanes were present and elemental analysis showed higher percentage of C, B in the oil. Main components in the oil were 10-undecenoic acid, oleicacid, octadecanonic acid, octadec-9-enoic acid, N-hexadecanoic acid, 3-phenyl-5-(pyridin-4-ylmethylidene)-2-thioxoimidazolidin- 4-one, Z-11-pentadecenal, oleanitrile, 9-octadecenamide, (z)-, methy; 12-hydroxy-9-octadecenenoate, 2-pentylnon-2-enal, methy; 12-hydroxy-9-octadecenenoate, 13-hexyl-oxa-cyclotridec- 10-en-2-one. Bio-oil's pH was 3.7 and calorific value is around 8500 kcal/kg.

Charles A. Mullen et.al had produced bio-oil and bio-char from pyrolysis of corn cob, corn Stover biomass in a bubbling fluidized bed of quartz sand at around 500 ^{0} C at feed rates 1.0 to 1.6 kg/h [2]. They found that corn Stover gave bio-oil yield of 6.6 %, slightly higher than that of Corn Cobs and calorific values are close at around 25 MJ/kg. Main components in corn cob bio-oil were water, acetol, acetic acid, levoglusan, and hydroxyacetaldehyde, whereas corn Stover bio-oil contain levoglocosan has highest concentration, followed by water, acetol, acetic acid, and hydroxylacetaldehyde. But, in many of the cases, the bio-oil obtained from pyrolysis have lower calorific value, higher moisture, oxygen content, greater viscosity and corrosivity than gasoline and diesel.is less quality compared to gasoline, diesel. So, there is need to upgrade these bio-fuels to use as transportation fuels.

2.4.Bio-fuel Upgradation

There are various methods to upgrade the bio-fuel. Those are:

- ✓ Catalytic pyrolysis
- ✓ Gasification of bio-oil
- ✓ Hydrotreating
- ✓ Esterification
- ✓ Catalytic cracking of bio-oil

2.4.1. Catalytic pyrolysis

Catalytic pyrolysis is carrying out pyrolysis of bio-mass in presence of heterogeneous catalyst. Heterogeneous catalysts are generally used in petroleum refineries for converting heavy oil fractions into lighter fuels.

Horne and Williams investigated the reaction of oxygenated biomass pyrolysis model compounds over a ZSM-5 catalyst in an attempt to simplify the problem [3]. They found that methanol could be catalytically converted to hydrocarbon products at temperatures 300–350 ^{0}C, whereas furfural, anisole, and cyclopentanone required higher temperatures. With the exception of anisole, increasing catalyst bed temperature reduced coke formation for the upgrading of the oxygenated compounds. The optimum catalysis temperature was 500–550 ^{0}C. At that temperature, however, anisole gave high yields of coke, suggesting that the phenolic compounds are the major coking components present in biomass-derived pyrolysis vapors.
Atutxa et al. studied the effect of an HZSM-5 zeolite on the in situ pyrolysis of sawdust at 400 ^{0}C [4]. With increase in catalyst mass, gas yields increased, whereas the liquid yield decreased notably. This is due to formation of CO_2 and CO by decarbonylation and decarboxylation. Liquid yields reduced due to decease in heavy liquid fraction and its transformation to water, lighter fractions and gases. The bio-oil produced resulted lesser char yields. The lighter fraction was more severely deoxygenated than the heavy fraction, which is evidence of the higher global reactivity of the compounds of the lighter fraction, especially of alcohols and acetic acid.

Adam et al. studied the pyrolysis of spruce wood biomass in a Py-GC–MS system in the presence of four different Al-MCM- 41-type catalysts (Si–Al ratio of 20) and modified Al-MCM-41 catalysts (by pore enlargement and introduction of copper (Cu) cations into the material structure) at 500 ^{0}C [5]. They found that after catalysis, the yield of acetic acid and furans increased and the yield of high molecular mass phenols decreased. Also, levoglocosan is absent in pyrolysis products. The overall yield of phenols increased and there was also a

slight increase of the hydrocarbon yield. The enlargement of the catalyst's pores reduced the yield of acetic acid and H_2O.

Thring et.al have pyrolysed lignin using HZSM-5 catalyst in the temperature range 500- 650 ^{0} C at different space velocities in a fixed bed reactor [6]. Their study shows that when lignin is solubilized in acetone and treated withHZSM-5 catalyst, it produces high yields of gasoline range hydrocarbons such as benzene, toluene and xylene. The liquid product fraction, which consists of mostly aromatic hydrocarbons, was maximized at 500 ^{0}C and a space velocity of 5 h^{-1}. On the other hand, the gas product consisted of olefins, light hydrocarbon gases, CO and CO2and was produced at the highest yield at 650 ^{0}C and a space velocity of 5 h^{-1}. Among the light hydrocarbon gases produced from the lignin, ethylene and propylene were the olefins produced in the highest quantities. Coke and char formation was particularly high at the low reaction temperatures. Depending on the reaction conditions, high selectivities were obtained as the lignin was largely converted to liquid fuels as well as other useful hydrocarbons.

Sanna et.al have catalytically upgraded spent grains using ACOL, RAWOL, ACSE, RAWSE, ALU in temperature range 370 – 520 ^{0} C in a fluidized bed reactor with a gas residence time of 6 seconds [7]. They observed that deoxygenating power of activated olivine (ACOL)>activated serpentine (ACSE)>alumina (ALU). They related catalytic activity to the increased surface areas of the materials owing to the structurally modified serpentine/ olivine phases after acid leaching and to the increased presence of metal oxides such as FeO, NiO, PdO on the surface. They also found that ACOL was found to be stable after a number of consecutive runs and its regeneration was possible without thermal treatment at high temperature.

Zhang et.al had compared catalytic and non-catalytic pyrolysis of corncob. They have used HZSM-5 catalyst in a fluidized bed reactors [8]. Among various temperatures and gas flow rates they obtained optimum conditions for maximum liquid yield at 550 ^{0} C, 3.4 L/min. On using catalyst, although oil fraction decreased, water, coke and gas yields increased and separation of water, oil and gas products was enhanced by multi-stage condenser system. Finally, they observed that bio-oil obtained from catalytic pyrolysis has more aromatics, calorific value and lesser oxygen content.

Ersan Pütünhad done catalytic pyrolysis of cotton seed in a fixed- bed reactor using Nitrogen as sweeping gas and Magnesium oxide catalyst [9]. At first, experiments were carried out at various temperatures in the range 400-700 ^{0}C to find the best temperature with gas flow of 100 ml/min, and heating rate 70 ^{0}C/min for 30 minutes using 5g catalyst and best yield obtained at 550 ^{0}C. In second phase, gas flow rates 50, 100, 200, 400 ml/min. The last phase was conducted

at 550 ^{0}C, 200 ml/min gas flow with different catalyst weight % of 5- 20. Their maximum oil yield was 48.3 %. They also observed that more gas flow rate gave higher liquid yield and increasing catalyst yields decreased oil yields and catalytic treatment halved the oxygen content of bio-oil.

2.4.2. Catalytic Cracking

Cracking is the name given to breaking up large hydrocarbon molecules into smaller and more useful bits. This is achieved by using high pressures and temperatures without a catalyst, or lower temperatures and pressures in the presence of a catalyst.

The source of the large hydrocarbon molecules is often the naphtha fraction or the gas oil fraction from the fractional distillation of crude oil (petroleum). These fractions are obtained from the distillation process as liquids, but are re-vaporized before cracking.

There isn't any single unique reaction happening in the cracker. The hydrocarbon molecules are broken up in a fairly random way to produce mixtures of smaller hydrocarbons, some of which have carbon-carbon double bonds. One possible reaction involving the hydrocarbon $C_{15}H_{32}$ might give ethane, propene and octane products [10].

The same technique can be used to convert heavier bio-oil components into lighter components, which are the main constituents in conventional gasoline, diesel.

Hew et.al had tried to found the optimum conditions for upgrading EFB- derived bio-oil [11]. They used Taguchi L9 technique for maximization of gasoline product. The temperatures are 350, 400, 450 ^{0} C, reaction times are 0.5, 15, 30 min and weight of catalyst 10, 20, 30 g for upgrading 250 ml of bio-oil in a high pressure reactor using ZSM-5 catalyst with initial Nitrogen purging. After the results were obtained S/N ratio was found for each run. Finally, the optimum conditions for cracking were identified as 400 ^{0} C, 30 g catalyst and reaction time 15 min, which yielded gasoline fraction of 91 .67%.

Adjaye et al. [12] studied the effect of mixtures of HZSM-5 and silica alumina on the product distribution during the conversion of maple wood to bio-oil and observed that the organic liquid that was produced with silica–alumina consisted mainly of aliphatic hydrocarbons, whereas the organic liquid product that HZSM-5 produced consisted mostly of aromatic hydrocarbons. The addition of HZSM-5 to silica–alumina reduced coke formation and increased organic liquid product and gas yields. The gradual increase of HZSM- 5 in the mixture changed the hydrocarbon products from aliphatic to aromatic. These observations suggest that the HZSM-5 is a more effective hydrogen transfer catalyst than the less acidic silica–alumina.

Lu et al. [13] used TiO2 Rutile, TiO2 Anatase, and ZrO2/TiO2 catalysts and their modified counterparts with incorporation of Ce, Ru, and Pd in a Py-GC–MS system for the upgrading of biomass pyrolysis vapors.TiO2 Rutile catalysts, especially the Pd-containing counterpart, exhibited very promising effect to convert the lignin-derived oligomers to monomeric phenols and favored the reduction of aldehydes and sugars, while increasing the ketones, acids, and cyclopentanones. The ZrO2/TiO2 catalysts reduced the phenol and acid yields remarkably, eliminated sugars and meanwhile, increased hydrocarbons, light linear ketones, and cyclopentanones.

Graca et.al have upgraded model bio-oil compounds containing major oxygenate groups such as acetic acid, phenol mixed with standard gasoil using industrial FCC equilibrium catalyst (E-CAT) and mixture of E-CAT and ZSM-5 [14]. They found that E-CAT gave higher conversion, lesser coke yields. Presence of higher phenol resulted in increase in gasoline and water yields, while acetic acid resulted in formation of CO, CO2 and light olefins. They concluded that compounds 10 wt. %, of oxygenated compounds can be processed in FCC units, excepting phenol.

Sharma et.al have upgraded whole bio-oil, pyrolytic lignin, and resid oil over HZSM-5 catalyst in temperature 340-410 ^{0}C in a fixed bed micro reactor [15]. They reported organic distillate fraction yields of 19 wt%, 30 wt%, 17wt% with whole bio-oil, pyrolytic lignin and resid bio-oil respectively. Aromatic concentration in those upgraded oils were 83wt%, 76 wt%, and 87 wt% [15].

Nokkosmaki et.al have upgraded the pyrolysis vapors of sawdust in a gas chromatograph using Zinc oxide in micro scale and bench-scale systems [16]. In micro scale system, pyroprobe was connected to gas chromatograph and pyrolysed at 600 ^{0} C. In bench-scale system, fluidized bed pyrolyser's side stream was connected to catalyst reactor with Zinc Oxide under Nitrogen atmosphere and NTP conditions. The vapors from reactor are connected to condensers to obtain liquid and gaseous products. On comparing with non-catalytic runs, they observed that ZnO was mild catalyst and suffered de-activation at 400 ^{0}C and also liquid yields doesn't vary much. The only improvement is improvement in viscosity of bio-oil.

Qiang Lu et.al have performed fast pyrolysis of poplar wood followed with catalytic cracking of pyrolysis vapors using Magnesium oxide, Calcium oxide, Zinc Oxide, Nickel Oxide, Titanium Oxide, Iron oxide catalysts [17]. They observed that eighty six compounds formed without catalysts, ZnO catalysis added six more compounds. They also observed that CaO catalyst significantly removed most of the primary pyrolytic products and favored formation

of linear ketones, cyclopentones and hydrocarbons. The remaining catalysts showed intermediate activity. They also observed that CaO gave highest yield of ketones, cyclopentenones, aldehydes, and phenols and it reduced formation of anhydrosugars and phenols.

Gayubo et.al (2004) have upgrade oxygenated bio-oil model components [18], [19]. With temperature rise, 1-propanal, 2-propanol have transformed to propene. Later, it transformed to C5+ olefins, butenes. With further increase in temperature, C5+ Paraffins, aromatics were formed. At 450 ^{0}C, propene, butenes and ethane formed finally. Butanol formed butenes at 200 ^{0}C, later they formed propene, C5+ olefins, C4+ paraffins and aromatics with increase in temperature. Finally, at 450 ^{0}C, butenes, propene and ethane formed. Methoxyphenol doesn't change much with temperature. Aldehydes doesn't transform much with temperature. They form little composition of C6+ olefins. Acetone transform to isobutenes at 250^{0}C, around 400 ^{0}C, C5+ olefins and propenes formed. With further increase in temperature, olefins transform to butane, ethane and aromatics transform to propene. Acetic acid transformed to acetone at higher temperatures. This is an auto catalytic reaction. Main oxygen removing mechanism is decarboxylation.

2.5.Motivation for the project

It will really a revolution to the world if bio-fuels are converted to commercial gasoline range fuels. But, it has been plagued by some limitations as mentioned earlier. Although many catalysts have been investigated, none of them gave required performance. Acidic catalysts like zeolites releasing high gaseous and producing more char, catalyst deactivation, mesoporous catalysts have lesser hydrothermal stability. Much work has been done using them and comparatively basic catalysts have explored to a lesser extent. In the literature, we observed that some authors reported that ZnO, MgO, Fe2O3 didn't have much catalytic activity than Cao. Also Cao is cheaply available all over the world. So, it would be very useful to further study the catalytic activity of Calcium Oxide on a variety of biomass and also by varying different parameters.

2.6.Objectives of project

Our objective is maximizing the formation and improving the quality of Organic liquid product yield from the Upgradation of bio-oil. We will define it based on parameters like temperature, catalyst weight, and atmosphere as:

1) To study the effect of catalyst mass on OLP yield.
2) To study the effect of reaction temperature on OLP yield.
3) To study the effect of inert atmosphere (Nitrogen) on OLP yield.

CHAPTER-3

EXPERIMENTAL SECTION

3. Experimental section

3.1.Feed stock

Castor seed biomass obtained from a local supplier.

Figure 4: Castor seeds

3.1.2. Feed stock characterization

3.1.2.1. Proximate analysis

The moisture content, volatiles, ash content, and fixed carbon are determined in proximate analysis primarily to ascertain the quality of the fuel [18].

Moisture content

It is found by measuring a known quantity of air-dried biomass ASTM D-871-82. Finely ground castor seed is kept at a temperature of 103 ^{0} C for one hour .Weight of the sample is measured before and after heating. The difference in weight is divided by initial sample weight to obtain moisture content.

Volatile matter

The volatile matter of a fuel is the condensable and non-condensable vapor released when the fuel is heated. Its amount depends on the rate of heating and the temperature to which it is heated. The applicable ASTM standard for determination of volatile matter is ASTM D-3157-07. 1g powdered sample is taken in a crucible covered with lid and kept at 950 ^{0} C for seven minutes. Difference of Weight of sample before and after heating is divided with initial sample weight to obtain the Volatile matter %.

Ash content

Ash is the inorganic solid residue left after the fuel is completely burned. Its primary ingredients are silica, aluminum, iron, and calcium; small amounts of magnesium, titanium, sodium, and potassium may also be present. Ash content is determined by ASTM test protocol D-1102. 1 g of sample taken in a previously weighed silica crucible and kept at a temperature of 750 ^{0} C in a muffle furnace for one and half hour. Weights of sample before and after heating are noted. Ash content is determined by dividing the difference of weight of sample before and after heating with initial sample weight.

Fixed carbon

This represents the solid carbon in the biomass that remains in the char in the pyrolysis process after devolatilization. It is determined by as:

% Fixed Carbon = 100- % Moisture - % Volatile matter - % Ash content

Table 2: Proximate analysis of Castor seed

Proximate analysis %	**Wt. (%)**
Moisture	25.37
Volatile matter	62.80
Ash	9.63
Fixed carbon	2.2

3.2.Catalyst

Calcium Oxide powder obtained from Rankem Chemicals.

3.2.1. Catalyst characterization

3.2.1.1.X-ray diffraction

X-ray crystallography is a tool used for identifying the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the

crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other information.

The catalyst powder was analyzed in a Rigaku japan ultima-iv analyzer and presented as below:

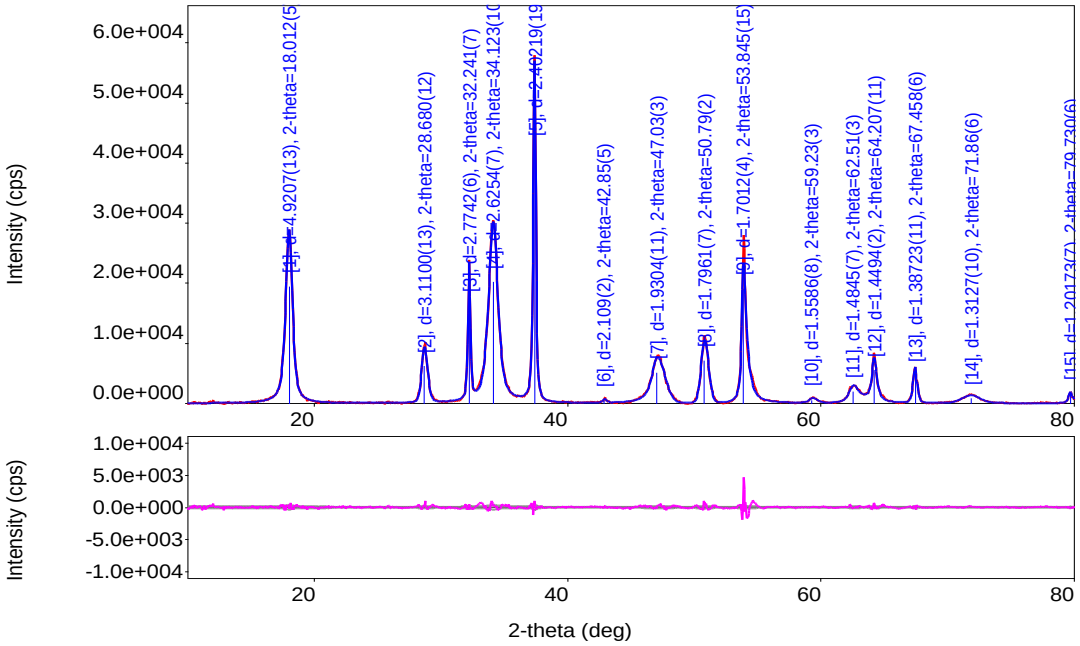

Figure 5: XRD peaks of CaO

Table 3: Peak list of XRD analysis

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
18.0620	8244.61	0.6000	4.90734	48.44
28.7059	2733.24	0.4200	3.10737	16.06
32.2407	6728.79	0.2400	2.77430	39.53
34.0241	8092.50	0.7200	2.63284	47.55
37.4045	17020.05	0.2400	2.40231	100.00
42.9568	208.74	0.1800	2.10378	1.23
47.1430	2058.73	0.3600	1.92626	12.10
50.8406	3287.14	0.4800	1.79450	19.31
53.9037	8163.68	0.3000	1.69953	47.97
59.3875	187.58	0.4800	1.55502	1.10

62.4364	501.03	0.8400	1.48621	2.94
64.1946	2174.57	0.4200	1.44968	12.78
67.4028	1657.89	0.3000	1.38826	9.74
71.7192	210.78	0.9600	1.31495	1.24
79.6702	354.60	0.2400	1.20250	2.08

3.2.1.2.SEM analysis

SEM analysis of Calcium oxide catalyst was carried in a Nova NanoSEM/ FEI at different magnifications to obtain micro structure of the catalyst.

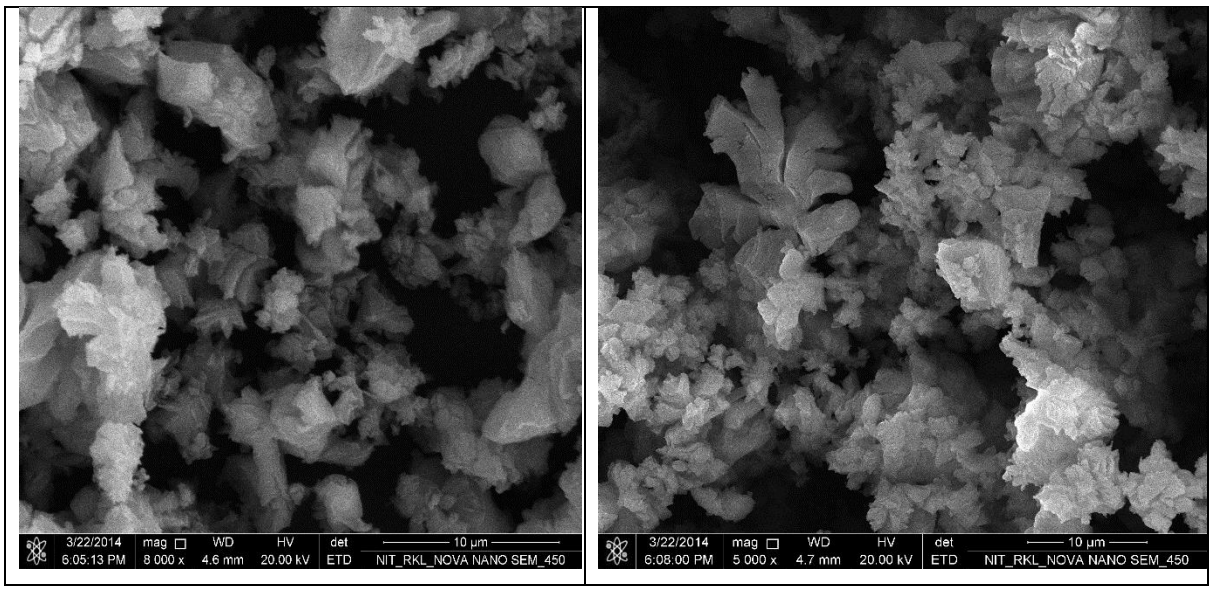

Figure 6: SEM analysis of CaO at magnifications 8000 X (left), 5000X (right)

3.2.1.3.EDX analysis

Energy-dispersive X-ray spectroscopy (EDX), is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on interaction of some source of X-ray excitation and a sample. Is known that each element has unique atomic structure and produce a unique set of peaks in X-ray spectrum. Using this principle, the elements are characterized in the sample. X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons (see PIXE), or a beam of X-rays, is focused into the sample to stimulate the emission of characteristic X-rays from the sample being studied. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energy of the X-rays are characteristic of the difference in energy between the two shells, and of the

atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured.

Table 4: EDX of Calcium Oxide

Spectrum: Sample 1 177

El	AN	Series	Net unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Ca	20	K-series	79108	59.14	64.28	41.81	1.76
O	8	K-series	3592	32.86	35.72	58.19	5.50
Au	79	L-series	790	0.00	0.00	0.00	0.00
		Total:		92.00	100.00	100.00	

3.3. Experimental setup

The experimental set up consists of PID controller, electrical heated furnace, pyrolysis reactor, glass condenser, nitrogen cylinder, rotameter and measuring cylinder. The temperature of the furnace was maintained by highly sensitive PID controller. Water is circulated as cooling medium in the condenser via a pump. The reactor is cylindrical shape vessel made up of stainless steel.

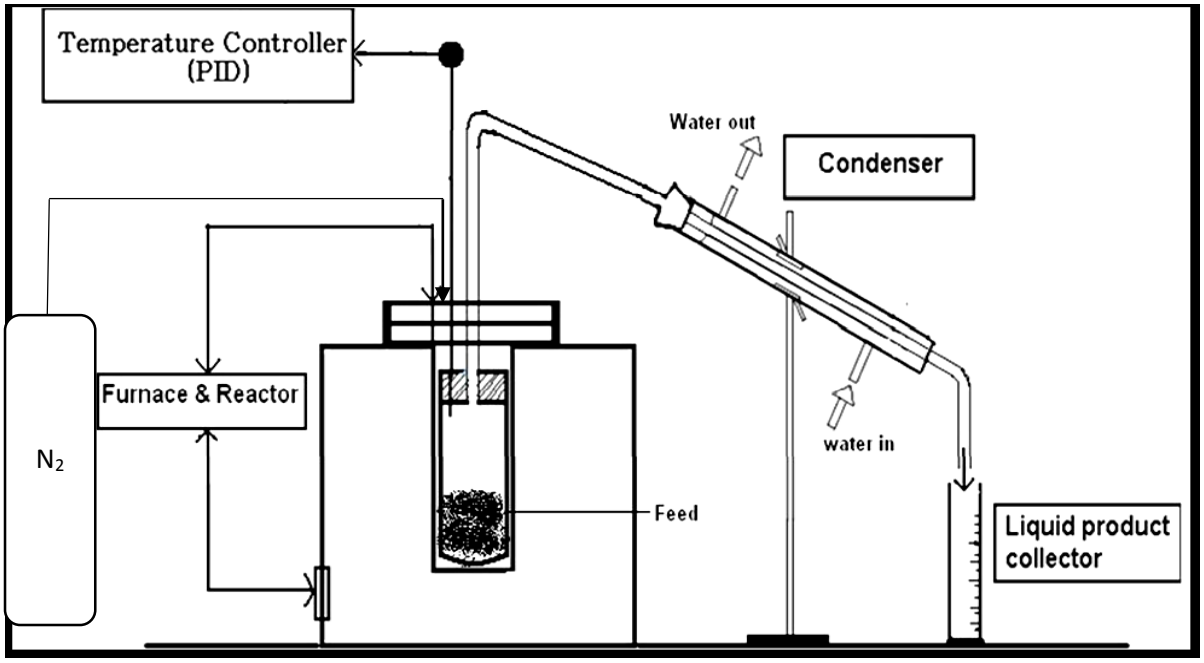

Figure 7: Experimental set up

3.3.1. Methods

Firstly, biomass is pyrolysed at 550 ^{0} C, as found in the paper R.K.Singh et.al [1]. The liquid product obtained is separated for aqueous and organic phases. The organic phase is collected and upgraded using Calcium oxide catalyst. The temperatures are 450, 500, 525 ^{0} C. Catalyst to Oil ratio was chosen as 1:12 (7.69 weight %), 1:9 (10%), 1:4 (20%). A total of eighteen runs, nine in Nitrogen, nine in ambient atmosphere were carried out as per the objectives.

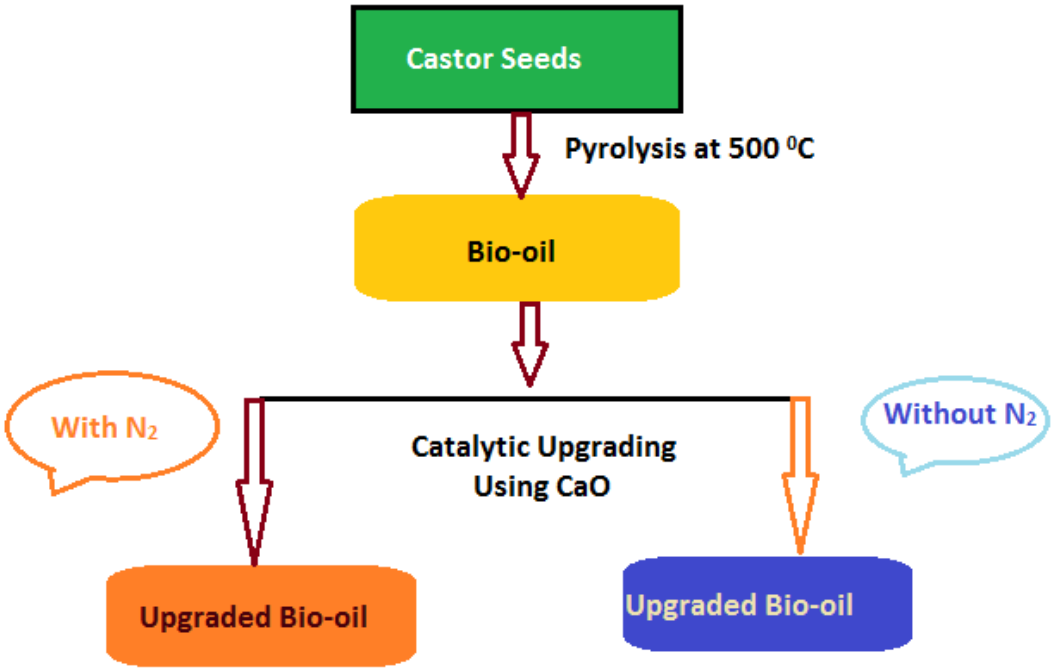

Figure 8: Methodology of project

CHAPTER-4

RESULTS AND DISCUSSIONS

4. Results and discussions

The yield of total liquid and OLP are chosen as key parameters used to describe the effectiveness of upgrading process. They are defined as:

$$Total\ oil\ yield\ \% = \frac{Weight\ of\ total\ liquid\ obtained}{Weight\ of\ bio-oil\ charged\ in\ reactor} \times 100$$

$$OLP\ yield\ \% = \frac{Weight\ of\ OLP\ obtained}{Weight\ of\ bio-oil\ charged\ in\ reactor} \times 100$$

4.1.1. Effect of temperature

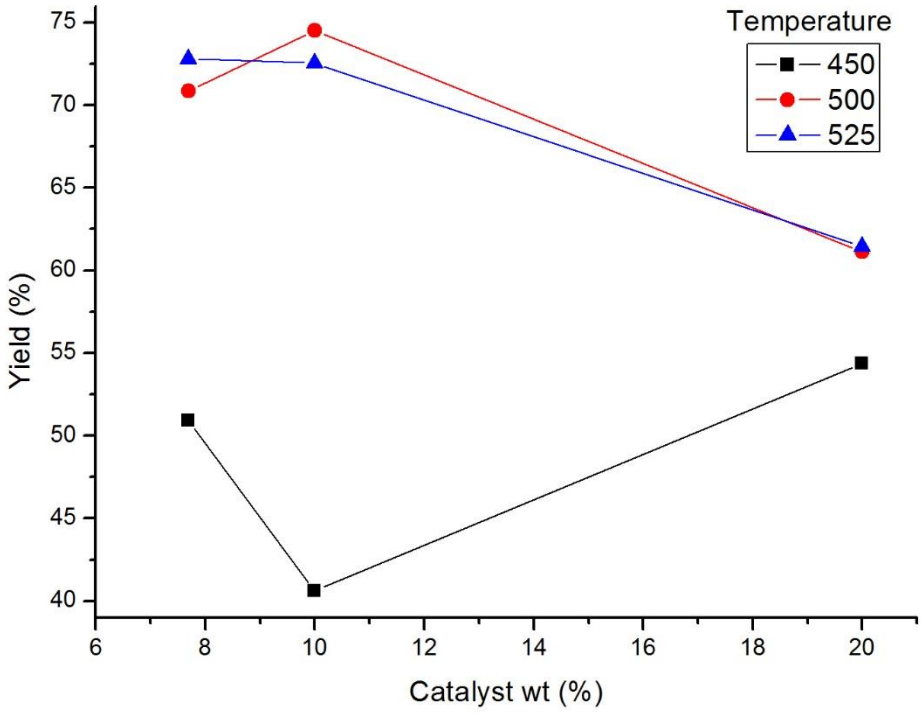

Figure 9: Effect of Temperature on Total liquid yield

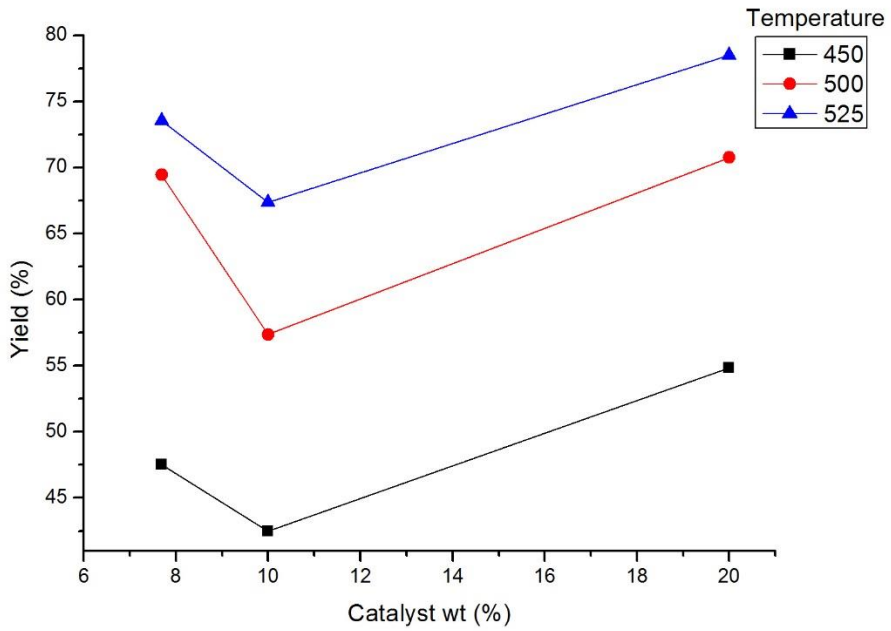

Figure 10: Effect of Temperature on Total liquid yield without Nitrogen

At any catalyst ratio, higher temperature resulted in higher yields. This is due to increased catalytic activity at higher temperatures.

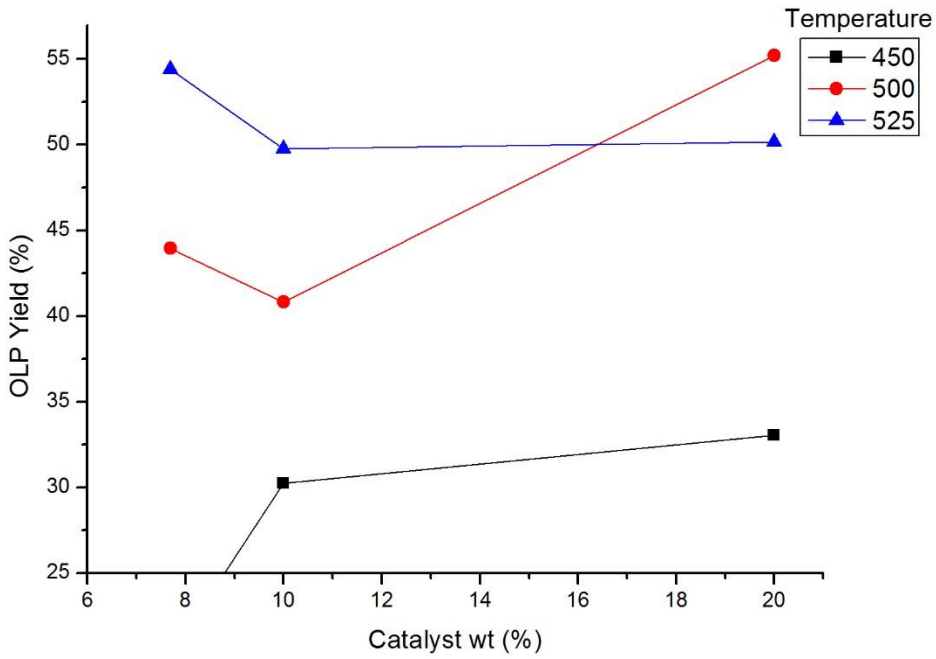

Figure 11: Effect of Temperature on OLP yield

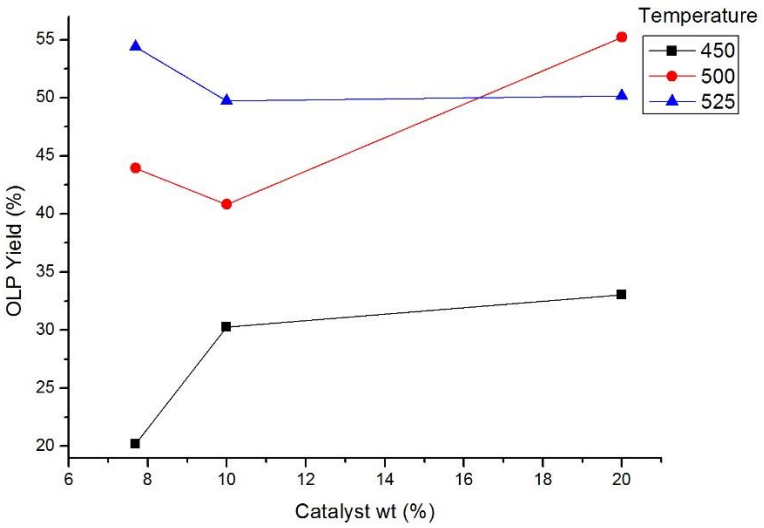

Figure 12: Effect of Temperature on OLP yield without Nitrogen

At any catalyst weight, increase in temperature resulted in higher OLP yields. This may be due to higher catalytic activity at higher temperatures. In case without Nitrogen purging also, OLP yield increased with temperature. These are in accordance with findings of Horne et.al [3] and Hew et.al [11].

4.1.2. Effect of catalyst Weight %

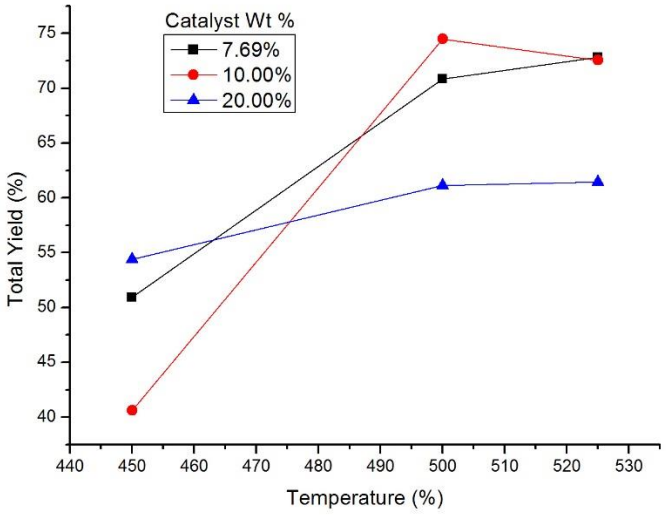

Figure 13: Effect of catalyst weight on Total liquid yield

At 450 ^{0}C, catalyst weight 10% gave lesser yields than 7.69%. This is not an expected trend. The reason may be the complex chemical nature of bio-oil. After Upgradation, aqueous and

organic layers are obtained. Generally aqueous layer is denser than organic layer. The 10% catalyst weight might have caused higher yield of denser aqueous layer, which might have resulted in decrease of overall liquid yield. At higher temperatures, 20% catalyst weight has given lesser liquid yields due to more gas formation, as stated by Atutxa et.al [4].

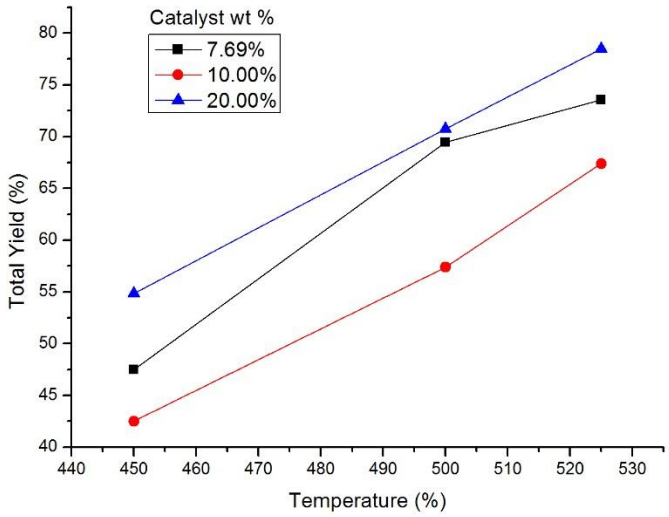

Figure 14: Effect of catalyst weight on Total liquid yield without Nitrogen

In Nitrogen atmosphere, catalyst weight of 10% gave least yield of total liquid. This may be attributed to complex chemical nature of bio-oil. It consists of many compounds like alcohols, carboxylic acids, alkenes, ketones etc... Each of the compounds have different selectivities to catalyst at different temperatures. It was described by Gayubo et.al [19], [20].

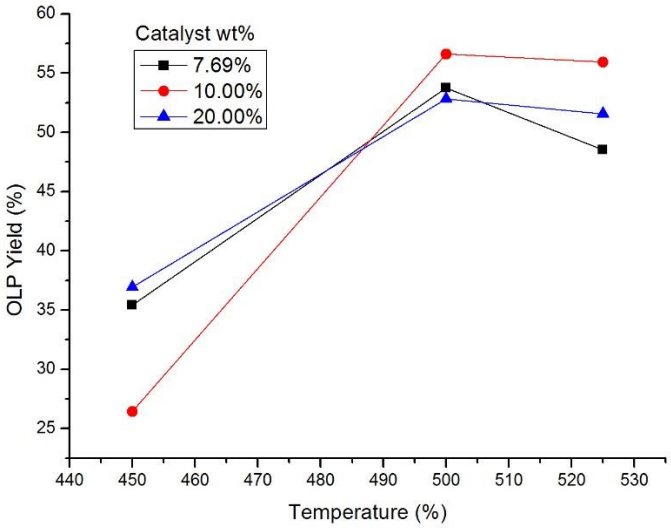

Figure 15: Effect of catalyst weight on OLP yield

At 450 ^{0}C, OLP yield is lesser for 10% catalyst weight. This might be due to higher char yields at low temperatures. At higher temperatures, OLP yield is nearly same for all catalyst ratio.

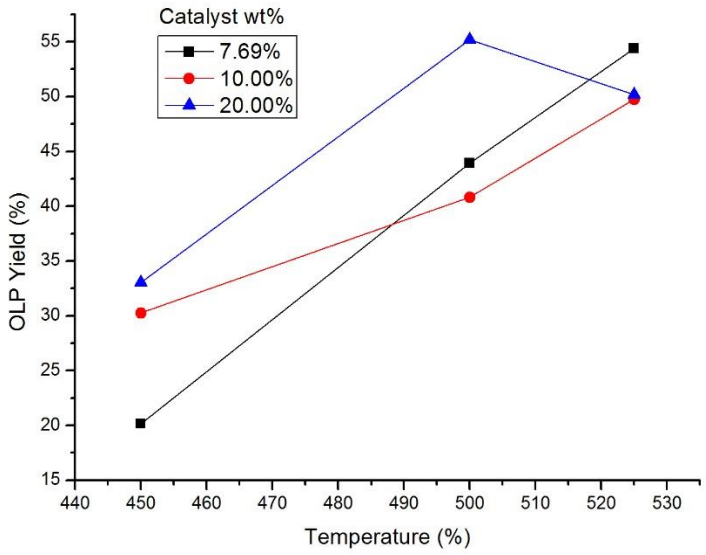

Figure 16: Effect of catalyst weight on OLP yield without Nitrogen

In this case, more catalyst weight gave higher OLP yields and difference in yields is less pronounced at higher temperatures.

4.1.3. Effect of Nitrogen purging

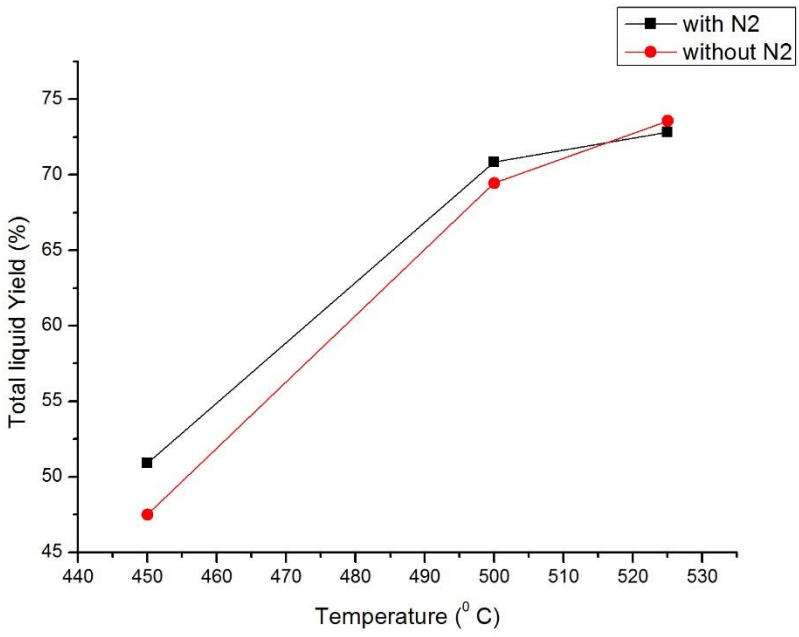

Figure 17: Effect of Nitrogen flow on Total liquid yield at catalyst wt. 7.69%

At 7.69% catalyst weight, higher oil yield obtained with Nitrogen. Highest yield obtained at 525 ^{0}C, but it doesn't vary much from 500 ^{0}C.

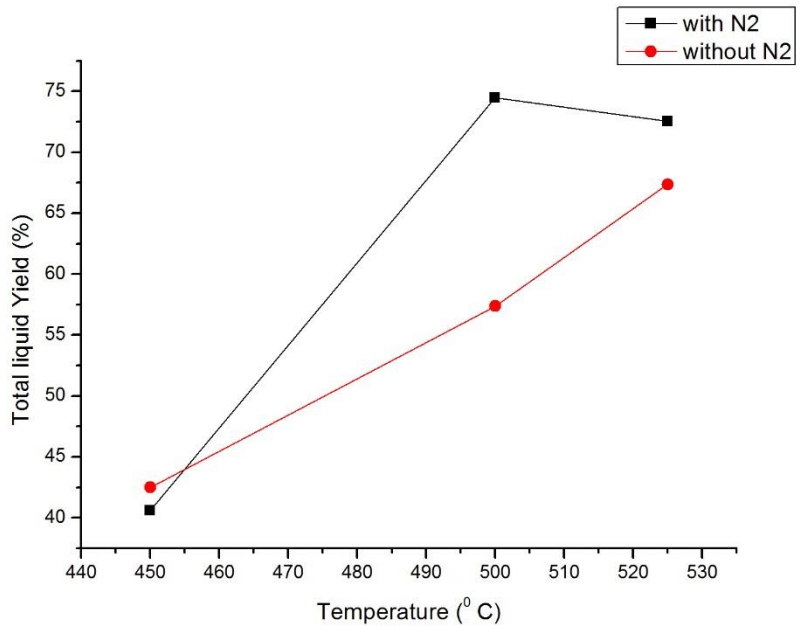

Figure 18: Effect of Nitrogen flow on Total liquid yield at catalyst wt. 10%

In catalyst weight 10 % also, Nitrogen purging gave better yields, but highest yield observed at 500^{0}C. At lower temperatures, Nitrogen purging resulted in lesser yield than ambient conditions.

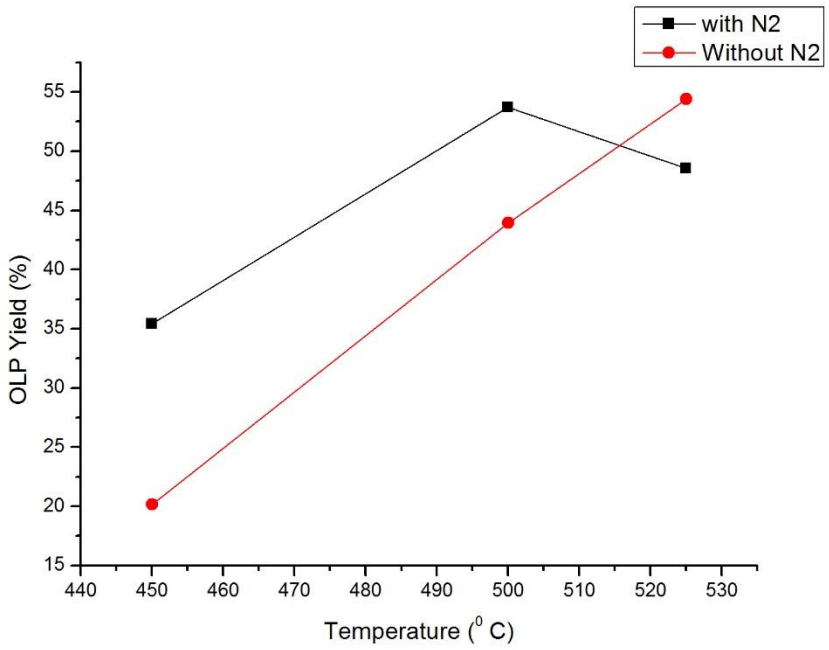

Figure 19: Effect of Nitrogen purging on OLP yield at catalyst wt. 7.69%

At 7.69 % catalyst weight and Nitrogen purging, OLP yields were recoded high up to 500 ^{0}C, and the difference is also high.

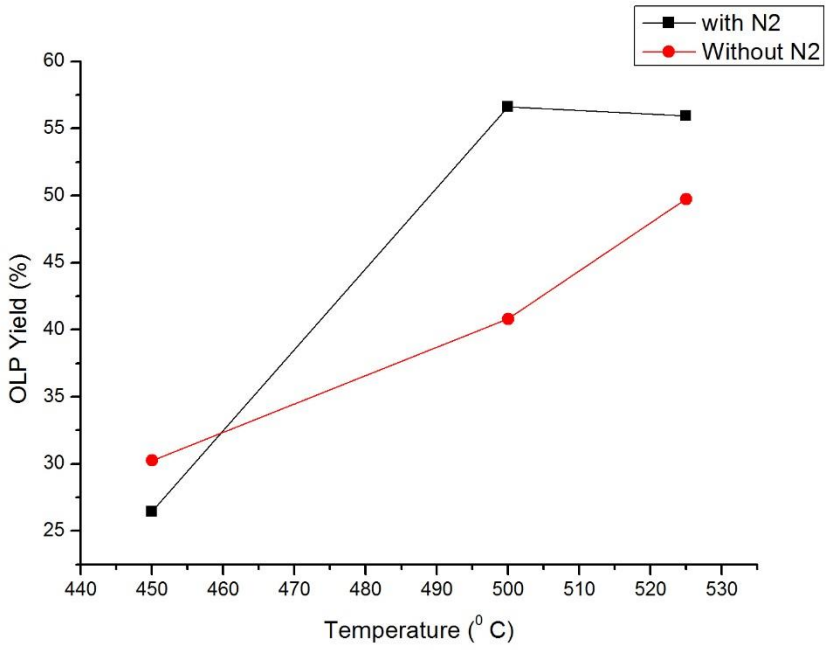

Figure 20: Effect of Nitrogen purging on OLP yield at catalyst wt. 10%

Nitrogen purging resulted in highest OLP yield at 500^{0}C, later decreased which may be due to secondary reactions.

4.2. FTIR analysis

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. The term Fourier transform infrared spectroscopy originates from the fact that a Fourier transform (a mathematical process) is required to convert the raw data into the actual spectrum.

FTIR analysis has been used to identify functional groups in the bio-oil.

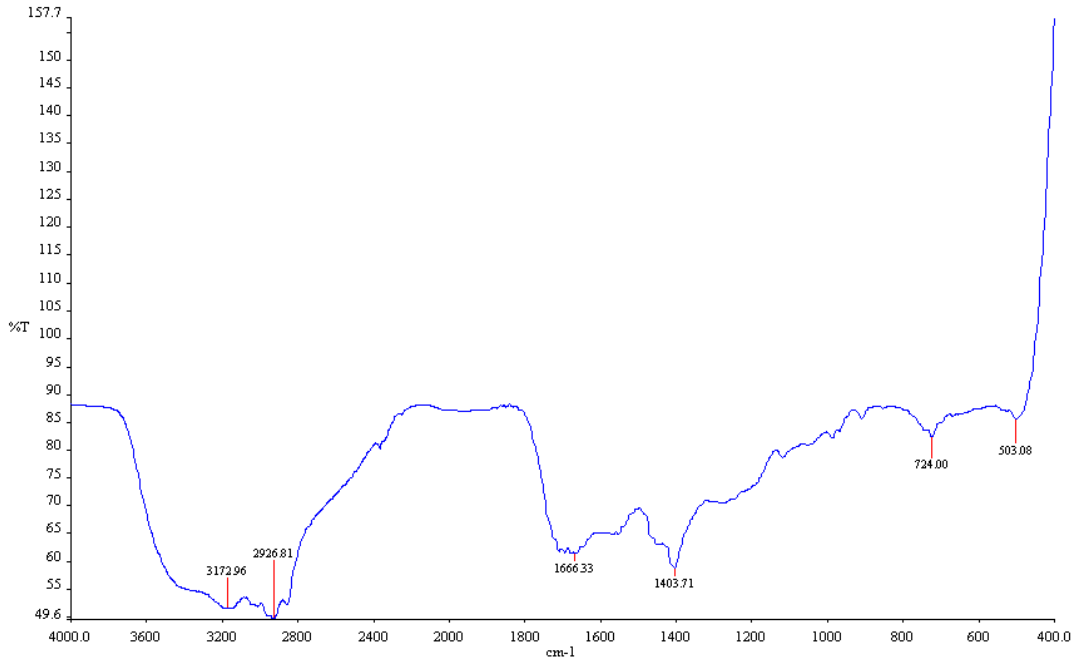

Figure 21: FTIR analysis of bio-oil

Table 5: Functional groups in bio-oil

Frequency range, cm^{-1}	**Bond**	**Functional group**
3600- 3100	Hydrogen bonded O-H stretch	Phenol, alcohols
3400-2400	Hydrogen bonded O-H stretch	Carboxylic acids
1750-1625	C=O Stretch	Ketones, Esters
1500–1400	C–C stretch (in–ring)	Aromatics
675-1000	=C-H bending	Alkene
690-515	C-Br stretch	Alkyl halides

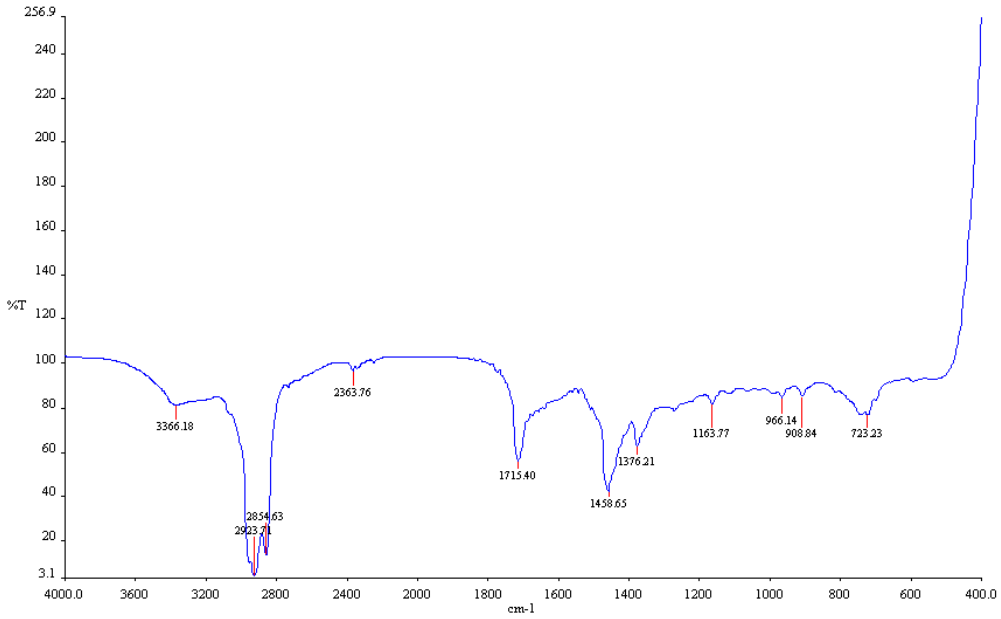

Figure 22: FTIR result of upgraded bio-oil at 450 ^{0}C, with N2, 10% catalyst weight

Table 6: Functional groups in upgraded bio-oil at 450 0C, with N2, 10% catalyst weight

Frequency range, cm^{-1}	**Bond**	**Functional group**
3500–3200	O–H stretch, H–bonded	Alcohols, phenols
3000–2850	C–H stretch	Alkanes
1715	C=O stretch	Ketones, saturated aliphatic
1470–1450	C–H bend	Alkanes
1300–1150	C–H wag (–CH2)	Alkyl halides
950–910	O–H bend	Carboxylic acids
900–675	C–H “oop”	Aromatics

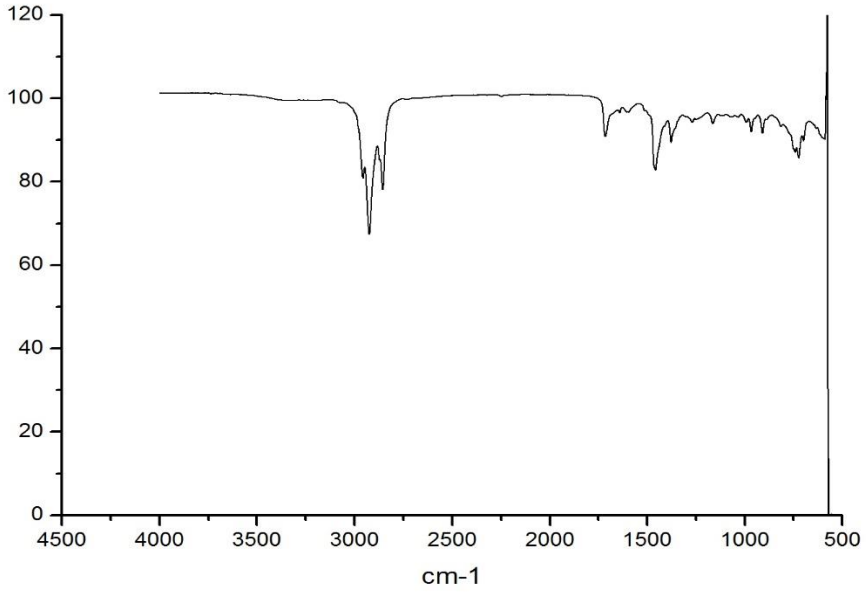

Figure 23: FTIR result upgraded bio-oil at 450 0 C, 10% catalyst weight, without Nitrogen

Table 7: Functional groups in upgraded bio-oil at 450 0 C, 10% catalyst weight, without Nitrogen

Frequency range, cm^{-1}	**Bond**	**Functional group**
3100-3010	=C-H stretch	Alkenes
1680-1620	C=C stretch	Alkenes
1600-1400	C=C stretch	Aromatic

4.3. Calorific value

Calorific value is determined in a Parr bomb calorimeter. The results are tabulated as:

Table 8: Calorific values

Bio-oil type	**Nitrogen**	**Temperature (^0C)**	**Catalyst weight %**	**Calorific value (kcal/kg)**
Raw bio-oil	--	--	--	6475.8
Upgraded bio-oil	Yes	450	10%	9636.6
Upgraded bio-oil	Yes	450	20%	9836.7
Upgraded bio-oil	Yes	500	10%	9844.6
Upgraded bio-oil	No	450	10%	9257.5

4.4. PH analysis

As basic catalysts were used it is expected that acidic nature of bio-oil be removed after Upgradation. They were tabulated as:

Table 9: pH values of upgraded bio-oils in presence of Nitrogen

Catalyst weight %	Temperature(^{O}C)	PH of bio-oil
7.692308	450	9.2
10	450	8.8
20	450	8.95
7.692308	500	9.29
10	500	9.36
20	500	9.74
7.692308	525	9.36
10	525	9.42
20	525	9.81

Table 10: pH values of upgraded bio-oils in ambient atmosphere

Catalyst weight %	Temperature(^{O}C)	PH of bio-oil
7.692308	450	9.05
10	450	8.68
20	450	9.55
7.692308	500	9.19
10	500	9.62
20	500	8.61
7.692308	525	9.44
10	525	9.36
20	525	8.66

CHAPTER-5

CONCLUSIONS

&

FUTURE WORK

5.1. Conclusions

- ✓ The highest liquid yield occurred at 525 ^{0}C, with 20% catalyst ratio, without Nitrogen. The second highest yield was also obtained without Nitrogen only.
- ✓ With or without, highest yields were obtained were obtained at 500, 525 ^{0}C. Yields at 525 ^{0}C>500 ^{0}C>450^{0}C.
- ✓ In OLP yields, using Nitrogen gave better results. This might be due to absence of oxygen which might have reduced secondary reactions.
- ✓ The highest OLP yield obtained at 500 ^{0}C, 10% catalyst weight and in presence of Nitrogen. This can be considered as the optimum temperature for upgrading castor seed bio-oil.
- ✓ Overall, Nitrogen purging gave better OLP yields than without Nitrogen, although total liquid yields are higher without Nitrogen purging.
- ✓ FTIR analysis revealed that after upgrading in Nitrogen, alkanes were formed. On the contrast, upgrading without Nitrogen resulted in elimination of Carboxylic acids, Ketones, and phenols.
- ✓ Calorific value hugely improved after Upgradation that too in presence of Nitrogen.
- ✓ PH analysis revealed that the acidity of bio-oil was completely eliminated. All the upgraded bio-oils registered pH values in the range 8-10. Thus, the stability of bio-oil improved a lot after Upgradation.

We have studied the effect of various parameters such as Reaction temperature, Catalyst weight percentage, and Nitrogen purging on the yields of total liquid, and upgraded bio-oil and also the conditions for maximum OLP yield. Hence, our project objectives have been fulfilled.

5.2. Future Work

- ✓ Total information on effect of temperature, catalyst, and Nitrogen purging can be obtained with GC-MS analysis.
- ✓ Energy consumption for Upgradation can be performed to verify the economic feasibility of Upgradation.

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